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[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM. No. 5.]

A STUDY OF THE ZIRCONATES.

BY F. P. VENABLE AND THOMAS CLARKE.

This class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl.¹ Of recent years several papers by L. Ouvrard² have appeared. The accounts given in the various text books of these zirconates are based upon the work of Hiortdahl or upon such abstracts of it as were to be found in the *Jahresberichte*, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watts and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained, dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses,

¹ *Ann. Chem. Pharm.*, 137, 34, 236.

² *Compt. Rend.*, 112, 144-46, and 113, 1021-22.

etc., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof that the zirconia was decomposed by the water. In the experiment 0.3910 gram zirconia heated with 0.3130 gram sodium carbonate to a dark redness for nine hours lost 0.1310 gram carbon dioxide, and on treatment with water 0.3871 gram "zirconia," or 99.03 per cent. was left. If an excess of sodium carbonate is used can one drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulas for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid and analyzes the residue, finding in it:

ZrO₂, 78.54 per cent.; Na₂O, 5.40 per cent.; and H₂O, 16.89 per cent., corresponding to Na₂O.8ZrO₂. He gets zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:

I. Fusing in boron trioxide the zirconia and the basic oxide (Ebelmen).

II. Fusing zirconia with alkaline carbonates, (Hiortdahl).

III. Fusing zirconia with alkaline hydroxides.

IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).

V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).

VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

I. FUSION WITH BORON TRIOXIDE.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

II. FUSION OF ZIRCONIA WITH ALKALINE CARBONATES.

The purified zirconia used had been dried at the temperature of the steam bath and therefore was not in the inactive condition brought about by igniting it at a very

high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his zirconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form, it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grams of zirconia were used in each case and a large excess of the carbonate. The amount of unattacked zirconia ranged from ninety-three to ninety-nine per cent., showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

I. WITH SODIUM CARBONATE.

Three experiments with sodium carbonate were carried to completion.

1. Two grams zirconia and eight grams sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 gram, or eight per cent. In this $ZrO_2=75.70$ per cent.; $Na_2O=24.30$.

2. Two grams zirconia fused with sixteen grams sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grams. Percentages: ZrO_2 , 74.18; Na_2O , 25.81. These correspond fairly with $(ZrO_2)_2(Na_2O)_3$.

3. Two grams zirconia fused with sixteen grams sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid 0.1220 gram, or six per cent. Percentages: ZrO_2 , 58.16; Na_2O , 41.84.

II. WITH POTASSIUM CARBONATE.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

III. FUSION OF ZIRCONIA WITH HYDROXIDES.

1. *Fusion with sodium hydroxide.*

Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grams zirconia fused with eight grams sodium hydroxide. Total amount dissolved, 1.1855 grams. An analysis, reduced to dry basis, gave ZrO_2 , 92.29, and Na_2O , 7.65.

2. Same amount taken as in experiment 1. Total amount dissolved 0.7655 gram, containing ZrO_2 , 93.19, and Na_2O , 6.22.

3. Two grams zirconia and sixteen grams sodium hydroxide. Amount dissolved 0.8004 gram, containing ZrO_2 , 92.57, and Na_2O , 7.38.

4. Two grams zirconia were fused with eight grams of sodium dioxide, instead of the hydroxide. Amount dissolved 0.7074 gram, and this contained 91.21 per cent. ZrO_2 .

$Na_2O.(ZrO_2)_6$ contains ZrO_2 , 29.30; and NaF_3 , 7.80.

$Na_2O.(ZrO_2)_7$ contains ZrO_2 , 93.29; and Na_2O , 6.79.

2. *Fusion with potassium hydroxide.*

These were carried out in a manner similar to those with sodium hydroxide and the action seemed to be about the same. In each experiment two grams of zirconia were taken and fused with sixteen grams of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 gram which contained 79.63 per cent. ZrO_2 ,

2. Dissolved 1.5241 grams which contained ZrO_2 , 82.98; K_2O , 17.00.

3. Dissolved 1.2078 grams which contained ZrO_2 , 78.59; K_2O , 21.40.

4. Dissolved 0.9297 gram which contained ZrO_2 , 85.51; K_2O , 14.49.

In analyzing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for ZrO_2 93.51, and Na_2O , 6.49, or very nearly the numbers gotten in experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it cannot be claimed from the analyses that definite zirconates have been prepared. Some allowance must be

made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(\text{Na}_2\text{O})_3(\text{ZrO}_2)_3$. In the fusion with sodium hydroxide the results range from $(\text{Na}_2\text{O})(\text{ZrO})_5$ [$\text{ZrO}_2=90.76$; $\text{Na}_2\text{O}=9.24$], to $(\text{Na}_2\text{O})(\text{ZrO})_8$ [$\text{ZrO}_2=94.08$; $\text{Na}_2\text{O}=5.92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from $(\text{K}_2\text{O})(\text{ZrO}_2)_3$ [$\text{ZrO}_2=79.57$; $\text{K}_2\text{O}=20.43$], to $(\text{ZrO}_2)_5(\text{K}_2\text{O})$ [$\text{ZrO}_2=86.74$; $\text{K}_2\text{O}=13.26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing ZrO_2 , 78.59 per cent., and K_2O , 21.41 per cent. was left. This nearly corresponds to the formula $\text{K}_2\text{O}(\text{ZrO}_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:

Two grams ZrO_2 were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis ZrO_2 , 89.11 per cent.; Li_2O , 10.99

per cent. Percentage of ZrO_2 calculated for $Li_2O \cdot 2ZrO_2$ is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia and gave the following results:

	I.	II.	Calculated for $CaO \cdot ZrO_2$.
ZrO_2	70.11	70.83	68.54
CaO	29.88	29.14	31.16

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analyzed with the following result:

	Found.	Calculated for $BaO \cdot ZrO_2$
ZrO_2	55.51	55.95
BaO	44.49	44.05

This is a grayish white powder, very fine and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained:

	Found.	Calculated for $SrO \cdot ZrO_2$
ZrO_2	54.22	54.55
SrO	45.77	45.45

7. The magnesia (eight grams) and zirconia (two grams)

was heated together for about four hours and then treated in the same manner as the calcium fusion, *i.e.*, first leached with dilute acetic acid and then washed with water until free from magnesia. The residue gave evidence of being crystalline.

	Found.	Calculated for MgO.ZrO ₂
ZrO ₂	76.28	75.30
MgO.....	23.70	24.70

IV. FUSION OF ZIRCONIA WITH CHLORIDES.

This method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium and lithium. According to the latter they all gave zirconates of the form M_2ZrO_3 .

1. *Fusion with sodium chloride.*

There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When two grams of zirconia were fused with sixteen grams of sodium chloride, it was found that less than two per cent. had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than two-tenths of a per cent.

2. *Fusion with potassium chloride.*

No action was observable. When two grams of zirconia were heated a number of hours with an excess of potassium chloride and the mass then treated as above, only three-tenths of a gram had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. *Fusion with alkaline earths.*

Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent

decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths except where these chlorides are decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

V. PRECIPITATION FROM THE SOLUTION OF A ZIRCONIUM SALT BY MEANS OF AN ALKALINE HYDROXIDE.

Watts speaks of this method but no experiments are recorded. It seemed to us upon examination of the question that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally, it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It, therefore, seems to be quite useless to make analyses of the precipitates gotten with different degrees

of washing; especially as somewhat similar experiments were carried out under the next heading.

VI. THE SOLUTION OF ZIRCONIUM HYDROXIDE IN CAUSTIC ALKALI.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalis were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off and the amount of zirconia present determined.

A 50 per cent solution potassium hydroxide dissolved per cc	0.00233 gm.
33 " " " " " " " "	0.00097 "
25 " " " " " " " "	0.00075 "
12 " " " " " " " "	0.00009 "

In the case of sodium hydroxide there seemed to be a stronger solvent action.

A 33 per cent solution dissolves per cc.	0.00245 gram.
25 " " " " " " " "	0.0012 "
12 " " " " " " " "	0.0005 "

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralization with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a liter of water used.) The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxides with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed and then decomposed by the action of water during the washing, but it seems more probable that this is, as is true in the

case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with. This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, CaO.ZrO_2 , etc. The same is true of the magnesium compound. For lithium the compound obtained was LiOZrO_2 . For the alkalis it seemed to be possible to obtain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

DOUBLE ZIRCONATES.

Two attempts at the formation of double zirconates were made.

1. Potassium calcium zirconate.

About two grams each of zirconia, potassium hydroxide and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then on treatment with dilute hydrochloric acid nearly the whole residue went into solution. The analysis gave ZrO_2 , 67.21 per cent.; CaO, 31.06; K_2O , 1.11. This is a calcium zirconate, $(CaO.ZrO_2)$, with a small part of the CaO substituted by K_2O .

2. Potassium aluminum zirconate.

Two grams of zirconia were fused for eight hours with two grams potassium hydroxide and three grams of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid and the insoluble portion removed by filtration. The analysis gave ZrO_2 , 72.38 per cent; Al_2O_3 , 7.66; K_2O , 20.00. These experiments indicate the possible existence of double zirconates, and when time permits this point will be further examined.

RIVER ADJUSTMENTS IN NORTH CAROLINA.

W. J. WEAVER.

NOTE.—In presenting this paper I beg to acknowledge my indebtedness to the lectures of Prof. Collier Cobb, and to his work and that of Messrs. Chas. Baskerville, R. H. Mitchell and other members of the class engaged in advanced work in Physical geography; but the mode of presentation is my own and I alone am responsible for any short-comings it may have. As my paper was presented for the Kerr Prize in Geol-

ogy it has not even had the critical reading of the head of the department, and lack of funds prevents my presenting as many maps as were contained in the paper.

North Carolina is naturally divided in three sections: (1) The Eastern or Costal plain; (2) The Piedmont Section, and, (3) The Western or Mountain District.

The costal plain runs inland about 100 or 125 miles. "Its western boundry line runs from the western part of Warren through Franklin, Wake, Cumberland, Chatham, Moore, Montgomery, and Anson counties." The whole coastal plain belongs to the Quarternary system, with frequent expanse of the Eocene and Miocene of the Tertiary along the rivers and ravines. As we go inland the country rises about one foot per mile, but from North to South is almost level. Over the whole section the primitive rocks are covered with a deep stratum of earth, principally sand. Along the western border and river courses we find granite, slate, and other rocks sparingly distributed, but no rocks of any kind can be found any where else in the region. The section is made up of beds of clay and sand with vast quantities of shell imbeded in them. The upland soil is mostly sandy loam which yields very good crops. There are vast areas of sand that will not yield anything but pines. In fact we know that this whole region has in recent geological time been raised above the sea level.¹

The Piedmont Section begins on the western edge of the coastal plain and runs west to the borders of the Blue Ridge. It is a rolling prairie in the east and gets rougher towards the west, including some small mountain ranges, the Brushy, Pilot, and King's Mountain. The mountain chains of the western part of the Piedmont belt run northeast and southwest; and as the rivers pass them they form rapids and falls that give excellent opportunity for manufacturers.

1. Handbook of North Carolina, 1885, published by Board of Agriculture.

Though you would expect a very rough hilly country on the West you do not find it so. The slope on the eastern side of the Blue Ridge is much steeper than that of the West. West of the Blue Ridge we have a very large valley bounded on the East by the Blue Ridge and on the West by the Great Smoky Mountains. This valley runs northeast and southwest between the two mountain chains and composes the mountainous districts of North Carolina.

This area has principally crystalline schists and gneisses with patches of conglomerates, sandstones, and shales and limestone. Both the Smokies on the West and the Blue Ridge on the East presents an anticlinal structure; the latter often having its monoclinial member absent. The area was in all probability once covered by an eastern extension of the Paleozoic rocks of East Tennessee, the sandstones of the western district being probably Cambrian (Chilhowee or Potsdam), the patches of limestone probably Silurian, and the grits and shales farther East possibly Carboniferous.¹ I assume that the folding that produced the Appalachian System was, as in Pennsylvania, rapid enough to deform the river systems. It gave rise to four great systems in North Carolina. The first we may call the Deep River syncline. It had its head in Chesterfield County, South Carolina, on the North Carolina line and ran northeast into Virginia. The second had its head in Caldwell County, North Carolina ran east of northeast and joined the first in Virginia. This one may be called the Dan River syncline. The third had its head in Catawba County, North Carolina, and ran south into South Carolina. This may be called the King's Mountain syncline. The fourth, which we may call the Asheville syncline was rather a canoe-shaped basin with a length of about 150 miles and a width of 20

1. Professor Collier Cobb's Lectures on General Critical Geology 1893-94; see also Cobb's Map of North Carolina, 1887.

miles in Watauga county and 50 miles in Henderson. Its ends are in Virginia and Georgia, and it took a Northeast and Southwest course. It was probably a lake for a long time until it flowed over, most probably in Henderson county. We find evidences of shores in Transylvania county that were evidently made by a lake. These synclines and the rivers that occupied them may be seen on map (1) It can be seen from the map that the original drainage of western North Carolina was not as it now is. Yet the present rivers are in many cases in the original river beds. The original river of the Asheville syncline headed in the northwest with what is now New river, ran southwest and crossed near Boone into the head waters of Watauga river, ran along the head waters of Watauga, but in the opposite direction taken by the Watauga now, for a few miles and crossed into the head of what is now Linville river, ran down the stream for about 20 miles and crossed into Brush creek and then into Toe river. At this point Linville river now enters what is known as the gorge. This is a very deep valley that has been cut since the original drainage we are describing. The river that cut through this great plateau has captured the Linville river and led it through, but at the time we are describing this gorge did not exist and the natural outlet was through Brush creek as stated. The river continued down Toe river as far as the fork known as South Toe, and there it crossed the present gap known as the Toe river gap. Down Swannanoa to French Broad and up French Broad and out through Mud creek into South Carolina, thence to sea. The drainage on the southwest began with the Hiwassee river which has since been captured and inverted, and ran east or a little south of east to Valley river, up Valley river, across Red Marble Gap and into Nantehala river, down this to its junction with Tuckaseege river, thence up Tuckaseege and across what is now known as Road Gap, down Richland creek to Pigeon river, up Pigeon to the great bend and

thence across Hominy Gap and down Hominy into the French Broad, up French Broad and out through Mud creek into South Carolina. We have many of our rivers in the original river beds. The Hiwassee has been captured and inverted but it still occupies the old bed. The Nantehala and Tuckaseege still occupy their old beds though there has been considerable change, a part of the latter having been inverted.

We would expect to find in these inverted rivers evidence of it in their sluggish movement but we must remember that most of them have since their inversion been so much lowered that they are the roughest to be found. The Little Tennessee River has cut a gorge through the Great Smoky Mountains over four thousand feet deep and we could hardly expect a river to be slow and sluggish whose lower waters had been lowered so much. Likewise the French Broad from above Hot Springs is very rough owing to the same fact. On the northwest the New river was made by cutting into the syncline and leading a part of the original river out. In map (I) we see that it is about to cut into the syncline and capture a part of the original river. Its headwaters push forward into the syncline until it has captured the headwaters of the original river and inverted a small part of it. This inverted part having a greater fall will move the divide southwest by degrees; and this continues until it reaches the mountain ranges near Boone which on account of its structure marks its final divide. The next stream that cut into our original river was the Watauga. It cut through the Smokies from Tennessee and led off a portion, but did its best work in determining the divide for the other rivers. The strata not all being of the same hardness we can see why these captures went as far as they did and no farther. When New River was inverted it probably would have led out much more of the streams of the northern and middle portions of the basin but for the fact that there was a ledge of rock that outcropped

about the central part of Watauga county and ran entirely across the basin at that point. These rocks had no influence upon the streams until the streams had levelled the country down to them. Then they formed a natural divide and fixed definitely the headwaters of New River. The Watauga was probably captured by a westward flowing stream on the southwest of these and therefore could not capture any of the New River's headwaters. Further on the south of the Watauga and running parallel to it there is another outcrop of rocks which run across the basin and join the Blue Ridge at Grandfather's Mountain, thus fixing definitely the divide between Linville and Watauga rivers. From this divide the river which goes south is Linville, which runs in the channel occupied formerly by the original river. This channel has the highlands of the Blue Ridge on the south and east; and on the west there is a range of mountains which separate Linville and Toe River. Linville River now runs down this valley about twenty miles and then enters what is known as the gorge. The original river formerly passed over and went down Brush Creek, Linville gorge not having been cut at that time, to Toe and down Toe as far as where South Toe enters. The Linville gradually gnawed its way back through a vast plateau and tapped the original river, thus leading off a few miles of it. We will also note that Linville is the only river that captured a stream from this basin and led it out to the east, all the rest have been captured and led off to the west through the Great Smokies.

The next capture was that of the headwaters of the Toe by the Nolichucky. This led all the North Fork of the original river out except the Swannanoa which still retains its old position. As the Nolichucky cuts through the Smoky Mountains it gradually lowers its channel and lowers the whole of the river. As the Nolichucky cuts its way back it furnishes a shorter route to the lowlands and being shorter it has a more rapid current which cuts

its channel faster and the divide migrates eastward until it is finally permanently located at Toe River gap, all the waters of the northwest having been captured by westward flowing streams. The next capture I shall take up belongs to the southwest tributary of the original river. The Hiwassee originally formed the headwaters of the river that drained the southern end of the Asheville syncline and led its waters up to the French Broad and thence out by that river. It is almost if not quite impossible to determine which of these captures took place first and in what order the others followed, but I am inclined to think that the rivers of the northeast were captured pretty much in the order that I have treated them, i. e., the headwaters (New River) were captured first, then a new stream cut in and took another deal off the head and so on down; in the southwest it is most probable that they did take this order. Considering the amount of erosion that the Little Tennessee has done I think that that stream was the first one to cut through and make a capture, thus draining all the basin west of the Balsam Mountains. Later the Hiwassee was captured and inverted and now runs out the southwest end of the basin. We can see by comparing the sketch of the original drainage with the map of to-day that the capture would turn a large volume of water through the Little Tennessee's gorge and thus help to sink it very rapidly. This is most probably what happened. As evidence of capture and inversion in the Little Tennessee River we have several rivers coming into it like the barbs on an arrow; i. e. they show their former tendency to run the other way. The Hiwassee also has several branches coming in in that manner, as the Nattely River and Shoal Creek. In map (I) we can see the river system of the Asheville syncline as it originally was. We see the little Tennessee and the river that captures the Hiwassee just cutting through the Great Smoky Mountains and looking in upon their prey. They are moving their respective divides to the

east and this continues until the divides have moved to their present position, and by this time the Little Tennessee has captured and inverted all the waters west of the Balsam Mountains and the divide has moved to Road Gap where it stops on account of the rocks that outcrop here. The Hiwassee is gradually overcome and captured in a similar manner. This only leaves Pigeon in its original position and running over what we now call Hominy Gap to the French Broad, and on the west we see the river that is to capture it cutting through the Smokies and gradually capturing its headwaters until they are finally all captured and led out through the Smokies. The New Found Mountains form a barrier between this river and Hominy Gap—the bed of the original stream is still the lowest gap in these Mountains.

The creek that flowed from the gap to French Broad is Hominy Creek and since the days of the readjustment it has recaptured two of its old tributaries; i. e. the two small branches that once ran to Pigeon River, now run into Hominy Creek and thence to French Broad*. All these waters that originally found their way to the sea through the upper French Broad valley would have made a large valley and such we find to-day. This stream has been cut into and captured by a stream from the west thus inverting the French Broad from its original course. The French Broad from the mouth of Swannanoa to Brevard, a distance of about forty miles, is a very smooth, sluggish river, so slow in its movements that one can but notice it and compare it to other mountain streams that usually go so rapidly. This is evidence of an inversion which has evidently taken place. From Asheville west, the French Broad is noted for its beauty, which consists in its rough, rugged course over rocks and through gorges, winding its way through the Great Smokies into the Appalachian River. There is very little fall in the French Broad between Brevard and Asheville while between Asheville

* National Geographic Magazine, vol. I, no. 4. By Bailey Willis,

and Paint Rock there is a great fall. At Asheville the altitude of the river is about 2100 feet while at Paint Rock it is 1264, thus giving a fall of 181 feet to the mile. The town of Brevard is lower than Asheville but both towns are above the river. However I believe that there would not be a difference of many feet in the altitude of the stream at the two places. We can see from map of the original drainage the French Broad as it ran southeast, with the river that is about to capture it cutting through the Smokies and having their divide just east of the Tennessee line. As in the other cases the divide has migrated east and the western river has captured and inverted the French Broad and led it out to the west. This finishes up the Asheville basin or syncline. Now let us look at the others. The next one I will take up is the old Dan River syncline which I have described above. It has had two changes. First it has been cut into by the Yadkin which has led about 50 miles of the Dan River headwaters to the sea through its channels and secondly it has had numerous readjustments through its headwaters and those of John's River, a tributary of the Catawba. In the drawing of the original drainage, map (I), we can see the position of this syncline which originally extended into Virginia and met the Deep River syncline. In the drawing we see that the Yadkin is about to cut into the Dan and as soon as it cuts through it will take the waters to the sea because having a shorter distance to go it must have a greater fall and will hence take the Dan in preference to being captured. The Dan was thus turned from its course and led to the sea by the Yadkin. The present Dan River has a branch, Town Fork, that still follows the old bed. The headwaters of the Yadkin have extended themselves still further north and are now known as the Ararat River. We will now turn our attention to the captures made in the headwaters of the syncline; and this brings me to mention a fifth syncline in North Carolina which I had not noticed until after I had

begun my work on this paper. This syncline we may call the Round Knob syncline since Round Knob is in the syncline and near its head. It began in the west of McDowell and ran a little north of east through Burke and Iredell counties, and it is probable that it continued through Davidson, Randolph and Chatham and joined the Deep River syncline in the latter county although we have no definite evidence that it did. In Map (I) we can see the drainage of this syncline as well as the captures which its waters made on those of the Dan River Syncline. I was at first disposed to think that John's River had captured the branch of Yadkin called Yadkin and that later it had been retaken by the Yadkin, but upon examination I find that those branches near the head of the Yadkin come down from a high plateau and enter the Yadkin at right angles and I am convinced that the branch called Yadkin is merely conforming to the family trait and has never been captured by John's River. If we look at the branches now called John's River and Buffalo Creek we find they have the Yadkin family traits and they show they have been captured by John's River. As the Yadkin cut into and captured the Dan so the Round Knob Syncline has been cut into by the Yadkin and probably by the Catawba and its waters have not gone through the Deep River as they probably did at first. Third Creek is probably nearest the old channel that traversed Round Knob Syncline. The Catawba that cut into the Round Knob Syncline ran a little east of the King's Mountain Syncline originally and it was its tributaries that cut through the eastern side of this syncline and led its waters out. The River that originally occupied the syncline was most probably what we call West Fork of Catawba River. This joined the Catawba where it passes to South Carolina. We see from the original diagram that the tributaries of the Catawba are about to cut through the eastern border of the King's Mountain syncline and lead its waters to the Catawba, and as time

passed we see they kept pushing to the west until they have obtained the position they now occupy. Dutchman's Creek has cut through and branched in the syncline and now drains the whole of it. West Fork of the Catawba which was originally in the syncline has cut through the western border and now drains a large area northwest of the syncline; thus in time the rivers have changed their positions and have so greatly eroded the syncline that we only find traces of it left, such as Anderson and King's Mountain on the west, and on the east not even so much, however we can trace its borders between Dutchman's Creek and Catawba.

The Deep River syncline headed in Chesterfield county South Carolina, and ran northeast to Virginia where it joined the Dan River syncline. We can see its position by turning to the general drainage Map of North Carolina after the Permian uplift, (Map I). Its eastern border still makes the fall line in our rivers, but its western borders were not so well marked, and did not have so definite a boundary. In fact the eastern border was a wide spread of country gradually sloping into it. The eastern border may be seen by drawing a line from Cheraw, South Carolina, northeast passing about ten miles east of Raleigh and striking the Virginia line where Dan river enters North Carolina. Along this line is an outcrop of a number of the older rocks, principally granite. (Hand Book of North Carolina, 1886.) And a little west of this is the old Deep River bed. The river headed in South Carolina with Brown's Creek and ran northeast to the Pee Dee River which formed a part of its bed, up what is now Little river, across to Wolf's Creek, down this to Deep river and down Deep river to Haw river where it turned up what now is New Hope river and across to Stone Creek, down this and up Knopf of Reed's Creek across to Tar river, up this, and to Fox Creek, over to Grassy Creek and down to the Dan river. At this time the coast line was only a few miles east of

this and the rivers such as Roanoke, Tar, Neuse, Cape Fear and others had not cut back to the syncline, however the distance to the sea was small and the fall was comparatively great and they were gradually cutting away. In drawing (Map 1) we can see how they cut this original deep river up and send their streams on westward for other adventures. The Great Pee Dee cut into the syncline near its head and led off Brown's Creek and inverted and led off Little river, then sent one of its streams on northwest and at last under the name of the Yadkin it cuts into the Dan River Syncline and captures a large part of its headwaters as we have described above. Cape Fear cuts into the syncline and leads off the part we now call New Hope and sends its branches on to help drain the territory northwest of the syncline (note the slowness of New Hope River). The Neuse cuts in and leads off a small portion as does the Roanoke, and thus helps the waters to find a shorter route to sea. At last this syncline leaves us this remnant of its former self as evidence of what it has been. The inverted creeks and rivers are yet at a loss to know what to do and so move along slowly, but by and by when they get accustomed to their new environment they will pick up their spirits and move along joyously as they did of old, and later generations will never know what a deal of trouble they have had. Their rate of flow is probably even now being accelerated by the lowering of the eastern border of the central plain.

REDUCTION OF CONCENTRATED SULPHURIC ACID BY COPPER.

BY CHARLES BASKERVILLE.

In a previous communication¹ the writer noted that copper was acted upon by concentrated sulphuric acid

¹This Journal, 17, 90.

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(1.84 sp. gr.) not only at the ordinary temperatures of the air, 20°-30°C., but at zero as well. Andrews¹ states that the assertion is incorrect and that it does not occur until the temperature 86°C. has been reached, or a point above the dissociation temperature of the concentrated sulphuric acid, 67°C. according to him. Andrews further says that the author's statements were based "not upon the demonstrations of the formation of sulphurous acid, but solely on the formation of copper sulphate," which, he says, occurs only "in consequence of the presence of the air." It is to be regretted that Dr. Andrews did not note carefully the statements of the author in his previous communication, as no reason whatever exists for any such conclusions, because it was distinctly stated that not only the copper as sulphate, but as sulphide was determined, as well as sulphurous acid, and moreover, that the experiments were carried out when the air had been replaced by a neutral gas, either hydrogen or carbon dioxide.

The author, although confident of the correctness of his former statement, carried out further experiments to correct the error, if committed or to establish, beyond question, the fact that concentrated sulphuric acid of 1.84 sp. gr. is reduced by copper below 86°C., the limit *positively* set by Dr. Andrews.

The fact that these experiments but confirmed the former statement of the author allows the incorporation of of the results in this paper.

As far back as 1838 the fact that copper is acted upon by concentrated sulphuric acid at ordinary temperatures, if sufficient time be given, was made known by Barruel². Calvert and Johnson,³ however, failed to obtain any action below 130° C., and considered that none took place.

¹ J. Am. Chem. Soc., 18, 253.

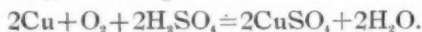
² J. de pharm., 20, 13, 1834.

³ J. Chem. Soc., 19, 438, 1866.

Pickering¹ however stated that "sulphuric acid attacks copper at all temperatures from 19° C., (and probably even still lower) upwards."

First Experiment.—Copper ribbon in strips, 1 x 3-4 cm., was submerged in concentrated sulphuric acid in a clean glass stoppered flask for a month. At the end of that time not only were there white crystals of anhydrous copper sulphate clinging to the sides of the containing vessel, but there was a very appreciable amount of brownish black cuprous sulphide and sulphur dioxide was easily detected by its strong odor when the vessel was opened.

Andrews² states "that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place according to the equation,



Formerly the author⁴ stated that the presence of the oxygen of the air when it comes into contact with the copper in the acid has great influence on the reaction. Fifty years ago, Maumené⁵ proved that when a current of oxygen gas was passed through the boiling acid, the amount of insoluble residue, *e. g.*, cuprous sulphide, was diminished, that is, less than there would be formed if the experiment were carried out with a current of carbon dioxide. The copper must be directly opposed to the oxygen by only partial submersion or the bubbling of the air against or around the submerged copper; but the air in a confined space, not at all in contact with the copper, but separated by a thick layer of concentrated sulphuric acid, has little or no effect.

Yet grant that the oxygen of the air (volume of air

¹ *J. Chem. Soc.*, Trans., 1878, 113.

² *J. Am. Chem. Soc.*, 18, 252.

³ *Ibid* 17-912.

⁴ *Am. Chem. Phys.* 1846 [3], 18, 311.

about 200 cc.) confined in the flask, had been utilized in the formation of the copper sulphate produced. According to the formula given above; the oxygen would be absorbed and no corresponding amount of any other gas would be eliminated; consequently there should a greater external pressure at the close than at the beginning of the experiment. When the smoothly fitting glass stopper was removed, not only no extra external pressure was noticed, but in fact a pressure from within. This was evidently produced by the sulphur dioxide generated. The sulphur dioxide was swept out by a current of air through a dilute solution of potassium permanganate, which was quickly bleached. The presence of sulphur dioxide was further proven by the addition of barium chloride to the bleached potassium permanganate solution. Nor does the formula given above account for the cuprous sulphide which is always produced.

Second experiment.—Realizing the possibility of some organic matter or dust remaining in the flask, although it had been carefully cleansed, the first experiment was repeated with the greatest precaution to ensure the absence of dust. The flask was scoured with boiling concentrated pure sulphuric acid containing potassium bichromate and carefully cleansed with distilled water. The last traces of water were removed by four subsequent washings with the same kind of concentrated acid used throughout the experiments. The experiment was carried out in the same manner as the first, the same results being obtained.

A blank experiment was carried out at the same time. The flask was rendered dust free in the manner just mentioned and fifty cc. of the same acid allowed to remain in the flask for six months. At the end of that period not a trace of sulphur dioxide could be detected in the blank, therefore the sulphur dioxide produced when the copper was inserted could not be due to the reduction of the sulphuric acid by an extraneous substance, but

solely by the copper. The conclusion is that sulphuric acid is reduced by copper when air is present at the ordinary temperatures, 20°-30° C.

Third experiment.—An ordinary Kjeldahl digesting flask was made dust free by the treatment noted above. 100 cc. sulphuric acid, 1.84 sp. gr., were placed therein and clean dry strips of copper ribbon were completely submerged in the acid. Now air-free carbon dioxide was passed through the flask for three hours. The inlet tube was just dipped into the acid. The flask was then attached to a suction pump, with a sulphuric acid drying flask intervening to prevent a possible return flow of gas or air which might carry moisture or dust into the flask. The flask was exhausted of the carbon dioxide present for three hours at a pressure of 150 mm. It was then sealed with the blast lamp and placed aside in a darkened cupboard. Observations were made every few days to note any reaction taking place. Within two days it could be easily seen that copper sulphate had been formed and the liquid was somewhat clouded by very finely divided suspended cuprous sulphide. Continued observations extending over a period of seven weeks showed only an increase in the amounts of both of these substances. The temperature of the cupboard had at no time risen above 20° C., and was for most of the time much lower. The flask was then opened as any other sealed tube, and instead of an external pressure inward, which had been sufficient to heavily dent the tube in sealing, there was a strong internal pressure outward. The gas evolved was sulphur dioxide, easily detected by its strong odor and bleaching effect upon a dilute solution of potassium permanganate. The sulphuric acid produced by the oxidation of the sulphur dioxide by the permanganate was precipitated by barium chloride. All solutions and apparatus were proven to be free from traces of sulphur dioxide and sulphuric acid by a blank experiment.

Conclusion.—Concentrated sulphuric acid, 1.84 sp. gr.,

is reduced by copper when air is absent and at temperatures far below 86° C., in fact at the ordinary atmospheric temperatures with the formation of copper sulphate and cuprous sulphide and the production of sulphur dioxide.

Finally.—Apparatus similar to that made use of by Andrews¹ with the modification of having three drying flasks containing concentrated sulphuric acid instead of one, and a Meyer absorption tube was substituted for a single small flask. These served merely as extra precautions against dust and insured an intimate mixing of the outgoing gases with permanganate. Within twelve hours the permanganate was bleached. Andrews' experiment lasted only fifteen minutes. The presence of the sulphur dioxide produced was easily detected by the odor when the apparatus was opened, and in the bleached permanganate solution by barium chloride. Copper sulphate and cuprous sulphide were formed.

Concentrated Sulphuric Acid is Acted upon by Copper at Zero.—Quantitative experiments were carried out by the author when the concentrated sulphuric acid in which the copper was submerged was practically at zero.² In stating the results, however, the author gave the temperature as " 0° – 10° C." The flask containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0° – 10° C., how-

¹ J. Am. Chem. Soc., 18, 251.

² Ibid, 17, 908.

ever. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except in regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

THE USE OF THE PERIODIC LAW IN TEACHING.

Read before Am. Asso. Adv. Science, Buffalo, August, 1896.

Only a few years after the announcement of the periodic law, when as yet it had attracted little attention, Lothar Meyer pleaded for its introduction by teachers of Inorganic Chemistry so that something of the orderliness observed in organic chemistry might begin to appear in the study of the inorganic elements. A casual examination of the text-books of the period and indeed of those for a number of years afterwards, would show the great need of some such system. Again the great German teacher twenty years later appeared before the Chemical Society at Berlin and threw the weight of the experience of these added years and all his enthusiasm in favor of a thorough use of the periodic system in teaching inorganic chemistry.

Some system must be adopted in teaching this branch of chemistry or the task is hopeless. What will you use if the periodic system is rejected? Some have answered this by using the old families where the elements are arranged by chemical analogies. Even in these families

the influence of the periodic law is deeply felt as any one can see by examining into their condition a dozen years ago and comparing it with the present. Still they are a most unsatisfactory guide to the truths of the science. Some have maintained that the periodic system was little more than those same old groups or families. That shows great ignorance, and a most superficial study of the periodic system. It does include all that was of value in the old groups but much more besides.

The history of the atomic theory is repeated in that of the periodic system. It is now meeting something of the opposition and even denunciation which the atomic theory met with in the third and fourth decades after its announcement. The unexplained exceptions to it are being magnified and many are inclined to think them insuperable and to look with doubt upon the entire system, while some are ready to throw it overboard as rubbish past its usefulness.

I do not think that in these classes of opponents will be found any who have made patient and thorough study of this system. To me, the more I study it the more its interest and value grows and the more fascinating the search after the great truths which unquestionably lie within it and of which it yields glimpses even in its incomplete state. For the system is incomplete. It cannot well be otherwise until our knowledges of the science is broader and deeper. It will grow with and direct the growth.

But in its incomplete state it is amply sufficient to act as a most helpful guide to the study of inorganic chemistry. It introduces order and clearness where such were previously, in large measure, lacking. It saves much useless repetition and so brings about conciseness and brevity, a saving that appeals to both teacher and pupil. There are few earnest students who will not become enthused with the wonderful symmetry of the science and hence of all nature when this Natural System is unfold-

ed to them. I have had a student come to me with the confession that he had been able to see nothing of the attractive beauty of the science in his study of it until this system brought law and order into what had only been confusion to him before.

The brief time allotted to me gives opportunity only for an earnest plea in behalf of the introduction of the system and does not admit of an extended exposition of the application. An excellent guide along this line will be found in the lecture of Lothar Meyer before the German Chemical Society which I have already referred to but let me say that the only truly successful way of teaching this system is for the teacher to make a faithful study of it and its capabilities for himself. It is not the old system of families and it is not to be treated merely as affording a convenient classification. All that was true in those groups it retains but it further develops and in a measure explains them.

A few of the lines of usefulness of the system may be pointed out. First arbitrary distinctions, such as between metals and non-metals, which have given chemists so much trouble to define and maintain, can be done away with. The Berzelian division into electro-positive and negative elements is revived and fixed and enables one to account for the gradations between these elements.

The system gives a simple, easily remembered and applied arrangement of valence in the place of the confusion and difficulties of the old methods.

The full introduction of the periodic system means a consecutive study of the elements as allied bodies. This in a measure resembles the study of the hydrocarbons in organic chemistry. It is very valuable as giving a connected view of these bodies. The symmetry of chemistry is better shown and the student feels that he has a grasp of the whole, an intelligent comprehension of the properties chemical behavior and inter-relations of the elements which he can scarcely arrive at by the old way.

When it comes to studying the compounds they are studied connectedly. Thus the hydrides of all the elements, are examined, giving their relation to hydrogen; then the oxides and the influence of the negative and positive nature of the elements upon their relation to oxygen and hydrogen. Under the head of each acid (for the acid largely determines the general characteristics of the salt) the various salts are discussed. This gives a better understanding of the characteristics, saves repetition and tends to fix in the memory the compounds or classes. And so too the constant taking up of the elements in their groups and series fixes them in the mind.

I cannot give the system in detail. Study the periodic system and Meyer's lecture carefully and then laying aside prejudices and traditions go boldly to work. What I have stated about the advantages of the system may seem overdrawn. The statements are based upon an experience of three years and no one has the right to gainsay them until he has faithfully tried the system.

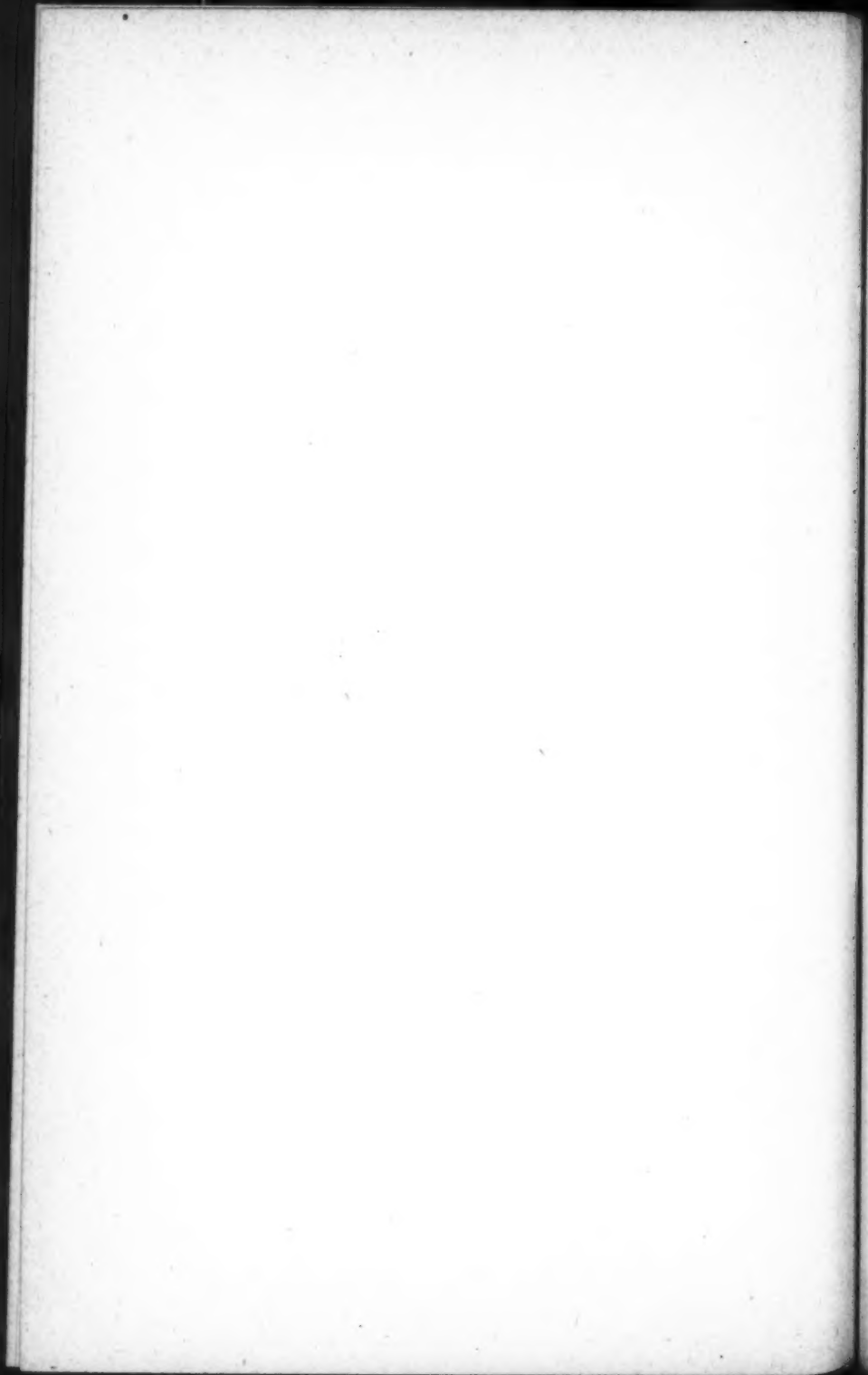




Fig. 1. Original Drainage.

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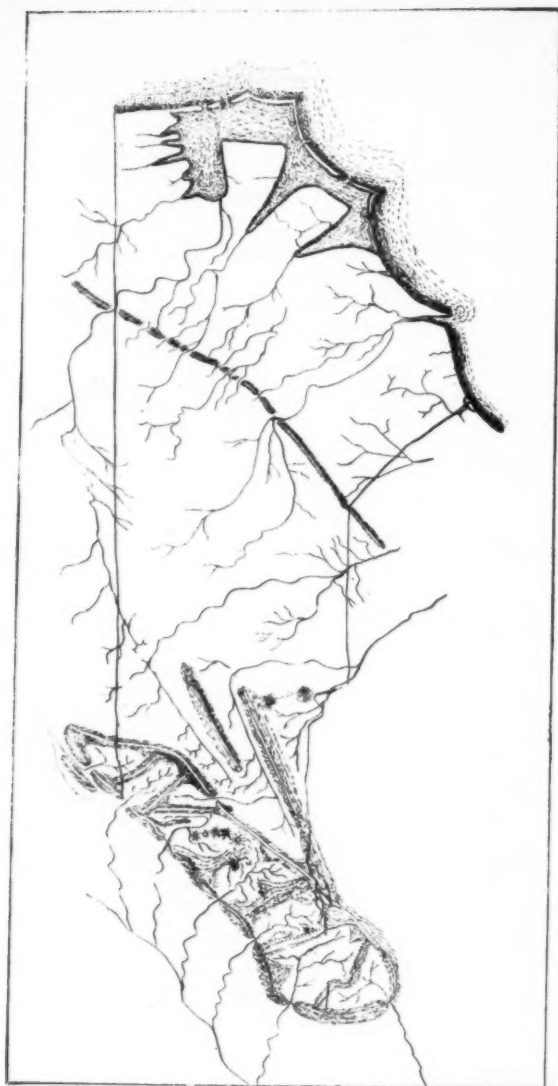
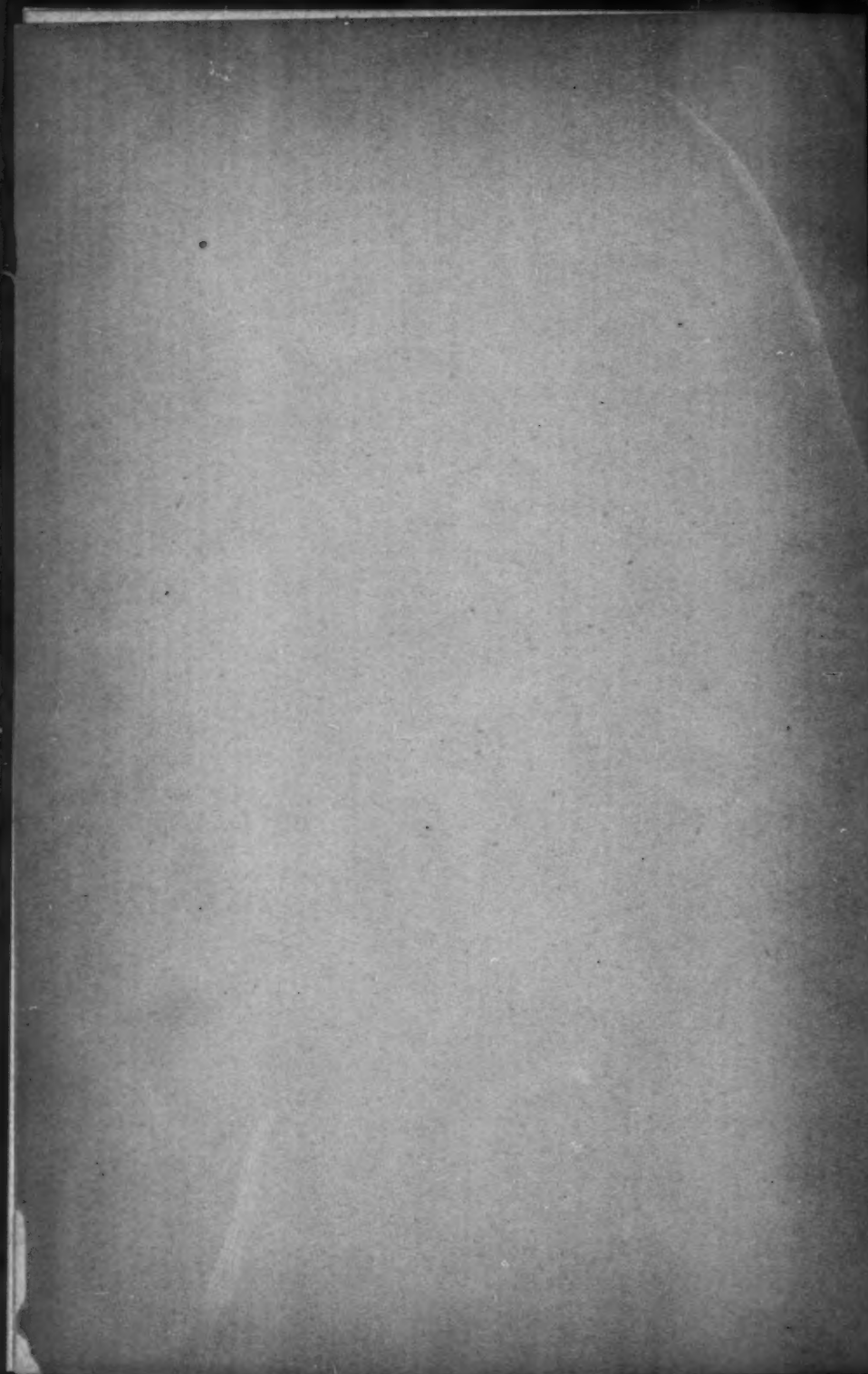


Fig. 2. Present Drainage.

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